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Synopsis

The crystal structure and phase transition of acetylene were studied by means of a low-temperature X-ray single crystal technique. The crystal showed a lattice transformation at about −140°C. The high-temperature modification was cubic with four molecules in a cell of the dimension $a=6.14$ Å at −117°C, the space group being T_h^6–Pa3. The parameters of carbon and hydrogen atoms were determined by the Fourier method. The molecular dimensions derived from the parameters were C≡C=1.20 Å and C—H =1.05 Å, the molecule being linear. The closest approach between neighboring molecules were H···H=3.28 Å and C···C=3.89 Å. Preliminary results of the low-temperature structure based on powder photographs are also described.

I. Introduction

Acetylene is the simplest molecule among the compounds having the carbon-carbon triple bond. The molecule is known to be linear, the linear dimension being about 3.3 Å. Its physical properties in solid or liquid state have scarcely been studied in detail because of its explosive property. Some experimental results concerning its crystal structure, however, can be found in literatures. Wahl(1) studied the phase transition of crystalline acetylene with a polarizing microscope, and observed a transition at about −185°C, that is, the crystal was isotropic in the range between the sublimation point (−84°C) and the transition point and was anisotropic at temperatures below the transition point. Later, Mooy(2) attempted to determine the crystal structure by the X-ray powder method. His experiments were carried out at the temperatures of liquid air (−185°C) and of liquid hydrogen, with the result that, at −185°C, the crystal was cubic with two molecules in a cell of dimension a=4.85 Å, while, at the liquid hydrogen temperature, owing to abnormal condensation of acetylene, good photographs sufficient to give a definite conclusion on the crystal structure were not obtained. At any rate, Mooy's results seem to be in accordance with those of Wahl. Another X-ray study was made by Washer,(3) who, in disagreement with the result by Mooy, concluded that acetylene crystallized in a system other than the cubic symmetry at −185°C. The main purpose of the present investigation is to see the inconsistency among these results of X-ray studies on the crystal structure of acetylene.

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* The 698th report of the Research Institute for Iron, Steel and Other Metals.

(1) W. Wahl, Proc. Roy. Soc., A **89** (1913), 327.

(2) H. H. Mooy, Comm. Leiden Phys. Lab., No. 223 (1932).

(3) F. E. Washer, Proc. Ind. Acad. Sci., **45** (1935), 222.

II. Experiment

1. Material

Acetylene was prepared by the reaction of calcium carbide with water. A reaction vessel with a special device for adding carbide to water was employed. The evolved gas was purified by passing successively through towers containing sulfuric acid, aqueous chromic acid, hydrochloric acid solution of mercuric chloride, nitric acid solution of copper nitrate and 50 percent aqueous solution of sodium hydroxide, and then dried over phosphorus pentoxide and finally condensed in a trap by means of liquid air. Further purification was effected by fractional sublimation under high vacuum. Vapor pressure measurements showed the purity to be satisfactory.

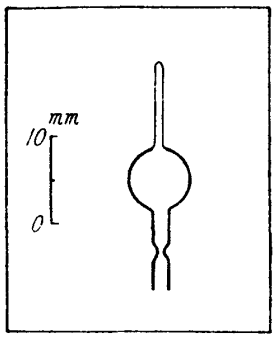

Fig. 1. Small gas holder with a thin walled capillary tube.

The purified gas was condensed in the capillary of a small gas holder shown in Fig. 1 and the tube was sealed off in vacuum. The liquid range of acetylene under atmospheric pressure is known to be very narrow.(4) For this reason, the growth of a good single crystal from the liquid was very difficult. The liquid range, however, became large when the gas was sealed in the holder under somewhat higher pressure than atmosphere. With this device, it was easy to get a single crystal extending over the whole length of the capillary.

2. Apparatus and procedure

The experimental method for single crystal X-ray study was, in principle, the same as that devised by Fankuchen(5) or Lipscomb.(6) The compressed air or nitrogen gas from cylinders was dehumidated and passed through a copper coil heat exchanger immersed in a Dewar vessel and then blown on the specimen through a vacuum jacketed glass tube. The small gas holder containing acetylene shown in Fig. 1 was mounted on the goniometer head of a X-ray camera. The temperature of the cold gas stream was controlled both by the level of liquid nitrogen in the Dewar flask and by the rate of flow. Temperature was measured with a copper—constantan thermocouple shaped into a small coil around the capillary of the gas holder. Using this apparatus, any temperature between room temperature and the liquid air temperature was obtained and could be kept constant within ±2°C under usual condition. By keeping the flow rate somewhat high, the formation of ice on the capillary

(4) D. McIntosh, Jour. Phys. Chem., **11** (1907), 306.

(5) H. S. Kaufman and I. Fankuchen, Rev. Sci. Instr., **20** (1949), 733.
B. Post, R. S. Schwartz and I. Fankuchen, Rev. Sci. Instr., **22** (1951), 219.

(6) S. C. Abrahams, R. L. Collin W. N. Lipscomb and T. B. Reed, Rev. Sci. Instr., **21** (1950), 396. The method of cooling the specimen by cold gas stream was devised originally by Mckeehan. L. W. Mckeehan, Proc. Nat. Acad. Sci., **8** (1922), 254.

surface was effectively avoided. Ice deposited on the periphery of the blowing pipe was removed mechanically, but it was usually not so much as to give some effect. Therefore, any device preventing the ice formation was not attached to the apparatus.

Single crystals of acetylene were prepared as follows: acetylene was first liquefied in the capillary by cooling it down to about −80°C and the temperature was then lowered very slowly to −85°C. A single crystal grew at about this temperature from the top of the capillary, its length being usually about 10 mm. The crystal was maintained for several minutes at a temperature slightly below the melting point and then cooled down to the desired temperature.

As will be described later, the acetylene crystal underwent a phase transformation at about −140°C. The high-temperature modification was cubic, the orientation of which, in general, could not be determined by any optical method. Therefore, the desired crystal axis was adjusted to the camera axis by the rotation or Laue photographs taken at about −100°C. As the direction of crystal growth was at random, it took a fairly long time to attain the desired crystal setting. Rotation and oscillation photographs about several crystal axes of the high-temperature modification were taken at −107°C and −117°C. For the low-temperature modification, rotation photographs were taken at about −150°C with the same apparatus as described above. Powder photographs at the liquid air temperature were also taken with a low-temperature powder camera.[7]

In these experiments, filtered X-rays from copper anode were always used. In single crystal works, a gyrating anode X-ray tube[8] was utilized to reduce the exposure time.

Relative intensities of the reflections were estimated visually by comparing them with several graded scales of standard reflections, the accuracy of which was believed to be considerably high. The intensities were carefully corrected for Lorentz and polarization factors. The absorption correction, however, was not necessary as the diameter of the specimen was less than 0.6 mm.

III. Crystal structure of the high-temperature modification

1. Unit cell and space group

In the following analysis, rotation and oscillation photographs about [100], [110] and [111] axes were used. The crystal was cubic and the lattice parameter at −117°C was

$$a = 6.14 \pm 0.01 \text{ Å} .$$

The assumption of four molecules in a cell leads to the calculated density of 0.745 at −117°C. Although the density of the crystal was not measured, that in the liquid state had been known to be 0.73 at −85°C.[4] Hence, the above assumption might be reasonable.

(7) T. Sugawara and E. Kanda, Sci. Rep. RITU, A 2 (1950), 216.
(8) I. Edamoto, *X-rays*, 3 (1941), 5. (in Japanese)

The extinctions are as follows: (okl) for k odd, (hol) for l odd and (hko) for h odd. The most probable space group is T_h^6.

2. Determination of the structure

Since the acetylene molecule has a center of symmetry, eight carbon and eight hydrogen atoms in the cell must be in two sets of 8(c) positions of the space group T_h^6. The coordinates of the 8(c) positions are

$$xxx;\ \tfrac{1}{2}+x, \tfrac{1}{2}-x, \bar{x};\ \bar{x}, \tfrac{1}{2}+x, \tfrac{1}{2}-x;\ \tfrac{1}{2}-x, \bar{x}, \tfrac{1}{2}+x;$$
$$\bar{x}x\bar{x};\ \tfrac{1}{2}-x, \tfrac{1}{2}+x, x;\ x, \tfrac{1}{2}-x, \tfrac{1}{2}+x;\ \tfrac{1}{2}+x, x, \tfrac{1}{2}-x;$$

therefore, the parameters to be determined are x_C and x_H of the respective atoms.

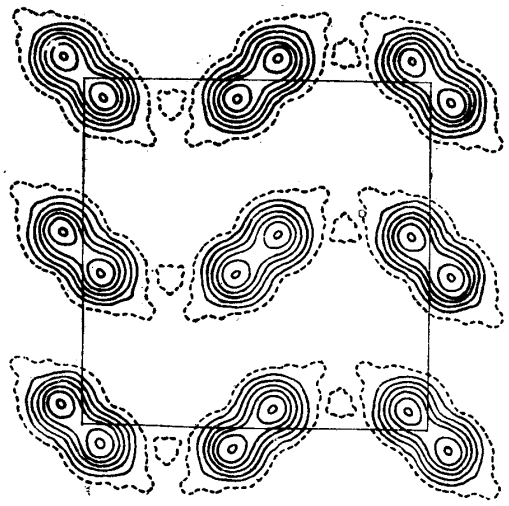

Fig. 2. Electron density projection on (001). Contours are drawn at the incervals of 1 electron/A^2, one electron line being dotted.

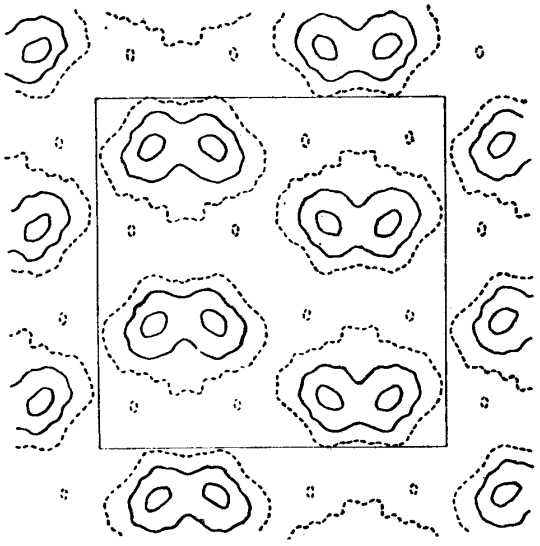

Fig. 3. Hydrogen contribution in the electron density projection on (001). Contours are drawn at the intervals of 0.25 electron/A^2, the 0.25 electron line being dotted.

The approximate value of the parameter x_C was first obtained by the trial and error method, assuming that the contribution of hydrogen atoms to the intensities would be small compared with that of carbon atoms. The agreement between the calculated structure factors and the experimental values was fair when x_C was 0.06. The refinement of the parameter value was carried out by the double Fourier series method using (hko) reflections. The electron density projection upon (001) is given in Fig. 2. It seemed probable to assign 0.056 for the parameter x_C of the carbon atom.

In the course of the trial and error analysis, somewhat large discrepancies between the calculated and observed structure factors were found in several low angle reflections such as (210). This might show that the contribution of hydrogen atoms should be considered to get better agreements between the observed and calculated structure factors. Moreover, small humps due probably to hydrogen atoms existed at the skirts of the carbon peaks in the projection illustrated above. These facts seemed to indicate the possibility of determining the positions of hydrogen atoms. Hence, the hydrogen contributions to the electron

density projection were synthetized by the double Fourier series method, in which Fourier coefficients $\{F_{obs}(hko)-F_c(hko)\}$ were used,[9] where $F_c(hko)$'s were the structure factors calculated with the carbon parameter alone. The result is illustrated in Fig. 3, which shows several diffuse peaks. The above coefficent contains two components, one of which is the hydrogen contributions to the reflection, the other the experimental error of the intensity estimation. Errors in the estimated intensities were considered to be small, because the estimations and corrections were carried out most carefully. Therefore, it would be most probable that the hydrogen atoms may be located at the apices of diffuse humps in the projection, and, accordingly, the parameter of the hydrogen atom was determined to be $x_H \sim 0.155$. A diagram of the structure thus determined is shown in Fig. 4.

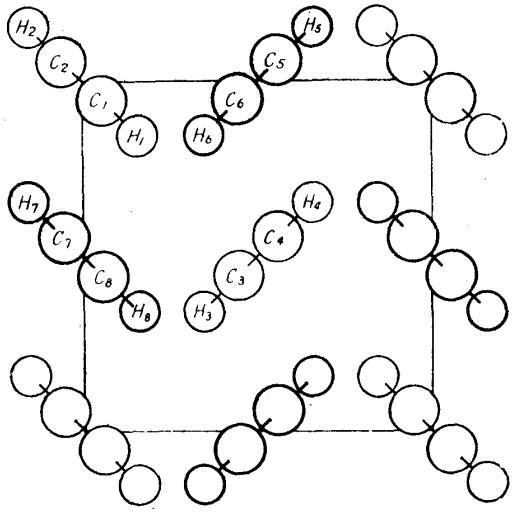

Fig. 4. Structure of the high-temperature modification projected on (001).

The structure factors were calculated on the basis of this set of parameters and were compared with the observed ones. The results are given in Table 1.

Table 1. Comparison of the observed and calculated structure factors.

hkl	F_C (calc.)	$F_{C,H}$ (calc.)	$\|F\|$ (obs.)	hkl	F_C (calc.)	$F_{C,H}$ (calc.)	$\|F\|$ (obs.)
111	+9.9	+10.2	10.0	333	+0.3	+0.2	<0.8
200,020,002	+8.6	+8.0	7.9	511,151,115	−0.5	−0.5	<0.8
210,021,102	−2.4	−3.4	3.5	502,250,025	−1.6	−1.4	1.5
211,121,112	−2.1	−2.6	2.8	432,324,243	−1.7	−1.7	1.7
220,202,022	+5.1	+5.2	5.2	423,342,234	−0.2	−0.2	<0.8
221,212,122	−1.4	−1.1	1.3	521,215,152	−1.4	−1.5	1.3
311,131,113	+3.2	+3.0	3.1	512,251,125	−0.1	−0.2	<0.8
222	+3.1	+3.0	3.2	440,404,044	0.1	−0.2	<0.8
302,230,023	−3.6	−3.7	3.6	522,252,225	−1.0	−1.1	1.5
321,213,132	−3.1	−3.1	3.3	441,414,144	−0.1	−0.2	<0.8
312,231,123	−0.7	−0.2	<0.7	433,343,334	−0.9	−0.9	0.9
400,040,004	+0.9	+0.6	<0.7	531,513,351	−0.2	−0.2	<0.8
322,232,223	−2.1	−2.1	2.0	315,153,135			
410,104,041	−1.7	−1.9	1.7	600,060,006	−0.9	−0.8	1.0
411,141,114	−1.5	−1.4	1.5	442,424,244	+0.1	0.0	<0.8
331,313,133	+1.0	+1.2	1.3	610,061,106	−0.5	−0.5	<0.8
420,402,240	+0.5	+0.6	0.7	611,161,116	−0.5	−0.5	<0.8
204,042,024				532,325,253	+0.2	+0.2	<0.8
421,214,142	−0.1	0.0	<0.7	523,352,235	−0.5	−0.6	<0.8
412,241,124	−1.0	−1.1	1.0	620,602,260	−0.6	−0.7	<0.8
332,323,233	−1.0	−1.0	0.9	206,062,026			
422,242,224	+0.3	+0.3	<0.8	621,216,162	+0.1	0.0	<0.8
430,304,043	−2.7	−2.7	2.5	612,261,126	+0.3	+0.3	<0.8
431,314,143	−0.5	−0.7	<0.8	450,504,045	−1.5	−1.5	1.4
413,341,134	−2.4	−2.4	2.5	443,434,344	−0.2	−0.2	<0.8

(9) This Fourier synthesis has been used for determining the positions of hydrogen atoms in a crystal. For example, W. Cochran, Acta Cryst. **4** (1951), 81.

Structure factors F_c calculated with the carbon parameters alone were in agreement with the observation except a few low angle reflections. The agreement is clearly improved by taking the hydrogen atoms into consideration (see, column $F_{C,H}$ of the table). The James-Brindley's atomic factor for free carbon atom was not adequate because of the distortion of the spherical symmetry in the electron distribution about the carbon nucleus caused by the carbon-carbon triple bond in the molecule. Therefore, the empirical atomic factor[10] of carbon in graphite was used with a slight modification as shown in Fig. 5. Of course, this includes a temperature factor in itself. The James-Brindley's value for the atomic factor of hydrogen was used with an arbitrary temperature factor $e^{-1.1(\sin\theta/\lambda)^2}$

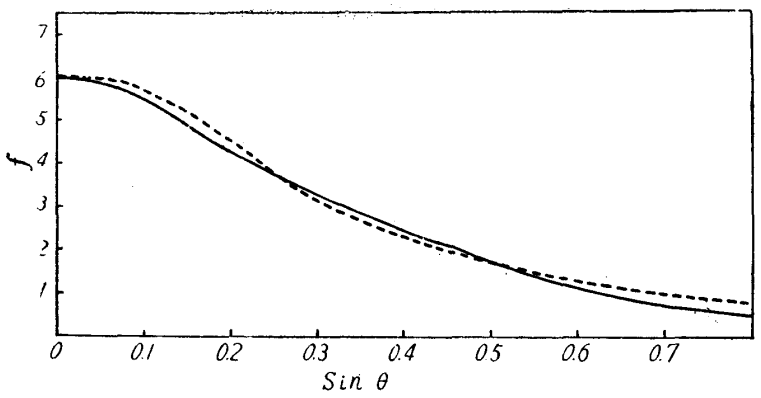

Fig. 5. Atomic structure factor for carbon. The dotted curve is the empirical atomic factor of carbon in graphite.[10]

IV. Low-temperature modification

When a crystal of the high temperature modification was cooled, a sudden change from transparency to opaque occurred at about −140°C. The photograph taken at about −150°C showed patterns different from those of the high-temperature modification. Powder photographs taken at −170°C, −180°C and −190°C were used for the study of the low-temperature modification. Any change in X-ray photographs was not observed between −140°C and −190°C. Powder lines were carefully corrected and submitted to analysis. The crystal seemed to belong to the orthorhombic system, though a definite conclusion on the structure could not be obtained.*) A comparison of powder patterns of the high and low temperature modifications are schematically shown in Fig. 6.

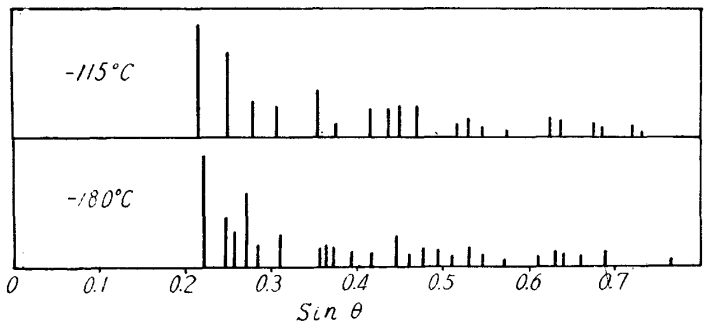

Fig. 6. Comparison of the powder lines of the high and low temperature modifications.

(10) K. Lonsdale, Proc. Roy. Soc., A 123 (1929), 494.

*) Recently, we have completed the structure analysis based on powder and single crystal photographs. Details will be published shortly.

V. Discussions

1. Structure of the high-temperature modification

Interatomic distances in the crystal of the high temperature modification are listed in Table 2.

The molecular dimensions are:

$$C-C = 1.20 \pm 0.02 \text{ Å},$$
$$C-H = 1.05 \pm 0.05 \text{ Å},$$
$$\angle CCH = 180^\circ.$$

The molecule is linear. The accuracy of the C−H bond distance is somewhat low because the positions of the hydrogen atoms could not be determined accurately by the Fourier methods.

The structure analysis of organic substances having carbon-carbon triple bonds has been performed only in a few examples. For the interatomic distance C≡C the followings are known: 1.19 Å for tolane[11] and 1.185 Å for diacetylene-dicarboxylic acid.[12] The C≡C distances of 1.195~1.204 Å have been found from the spectroscopic and electron diffraction studies of acetylene and the related molecules.[13][14] The value of 1.20 Å found by the present anthors in acetylene crystals is in good accordance with them.

The positions of hydrogen atoms in this crystal are of considerable interest. The determination of these positions in organic crystals by X-ray methods has been recognized to be difficult. Owing to the improvement of the techniques, however, it has been made successfully in such substances as sebacic acid and hexamethylene diamine.[15] The success in the present investigation might be due to the fact that the lengths of the C—H and C≡C bonds in an acetylene molecule were of comparable order. The calculated C—H distance of 1.05 Å is in agreement with 1.058~1.06 Å in literatures[13][14] within the experimental error of ±0.05 Å.

Table 2. Interatomic distances.

H_1——C_1 = 1.05 Å	C_1——C_2 = 1.20 Å
H_1……H_3 = 3.80 〃	C_1……C_3 = 3.95 〃
H_1……H_4 = 3.28 〃	C_1……C_4 = 3.89 〃
H_1……H_5 = 3.80 〃	C_1……C_5 = 3.95 〃
H_1……H_6 = 3.28 〃	C_1……C_6 = 3.89 〃
H_1……H_7 = 3.80 〃	C_1……C_7 = 3.95 〃
H_1……H_8 = 3.28 〃	C_1……C_8 = 3.89 〃
H_4……H_5 = 3.28 〃	C_4……C_5 = 3.89 〃
H_4……H_6 = 3.80 〃	C_4……C_6 = 3.95 〃
H_6……H_7 = 3.28 〃	C_6……C_7 = 3.89 〃

The closest H···H distance 3.28 Å between neighboring molecules found in the crystal was larger than 2.4 Å, twice the van der Waals radius of hydrogen in organic crystals.[16] This is not unreasonable, because Pauling's value of

(11) J. M. Robertson, J. Chem. Soc., **1945**, 249.
(12) J. D. Dunitz and J. M. Robertson, J. Chem. Soc., **1947**, 148.
J. D. Dunitz and J. M. Robertson, J. Chem. Soc., **1947**, 1145.
(13) G. Herzberg, F. Patat and J. W. T. Spinks, Nature, **133** (1934), 951.
(14) L. Pauling, H. D. Springall, and K. J. Palmer, J. Amer. Chem. Soc., **61** (1939), 927.
(15) J. D. Morrison, W. P. Binnie, and J. M. Robertson, Nature, **162** (1948), 889.
(16) L. Pauling, *The Nature of the Chemical Bond*, (Cornell Univ. Press, 1940), 191.

van der Waals radius for hydrogen gives only its order of magnitude. The closest C···C distance 3.89 Å are in good agreement with the van der Waals distance between CH_3 groups in organic crystals, which are between 3.9 Å and 4.1 Å.[16]

It is common that the high temperature modification of a crystal belongs either to the cubic system or to the hexagonal system due to the high degree of freedom of motions of molecules or atomic groups in molecules. The situation seems to have been realized in the present case. With respect to this fact, it is interesting to compare the crystal structure of acetylene with that of carbon dioxide.[17] Both crystals sublime at about −80°C.*) Their molecules are both linear and their vapor pressure curves are similar to each other. They crystallize both in cubic with the same space group T_h^6, and the features of molecular arrangement are alike. These facts are very suggestive of the relations between the molecular shape, intermolecular forces and the crystal structure.

2. Phase transition of crystalline acetylene

According to the present experiments, the acetylene crystal underwent a lattice transformation from the cubic to a lower symmetric system at −140°C, which was quite different from −185°C found by Wahl. The present result, however, seems to be correct, because the temperature measurement by Wahl was not reliable and because any phase change was not observed between −140°C and −190°C in our experiments. Therefore, Mooy's[2] conclusion on the structure of the high temperature modification, based on the powder photographs at −185°C, is not correct at all. His photographs at −185°C is rather in coincidence with our photographs of the low temperature modification in greater parts. On these bases, the present authors' results may be considered to be more reliable than those of the previous investigations by Wahl and Mooy.

Concluding remarks

The authors wish to express their thanks to Prof. I. Edamoto of Tohoku University who kindly lended us his original plan of the gyrating anode X-ray tube, and also to the members of the workshop in the Research Institute for Iron, Steel and Other Metals who designed and manufactured the X-ray tube.

A part of this work was aided by a fund from the Scientific Research Expenditure of the Department of Education.

(17) J. de Smedt and W. H. Keesom, Comm. Leiden, Suppl. No. 53a (1924).
W. H. Keesom and J. W. Köhler, Comm. Leiden, No. 230b (1934).

*) The sublimation points are −84.1°C for acetylene and −78.5°C for carbon dioxide.